2016

Investigation of Latex Resins for Use in Aerosol Coatings

Brian Robert Gosselin
Lehigh University

Investigation of Latex Resins for Use in Aerosol Coatings

by

Brian Gosselin

A Thesis

Presented to the Graduate and Research Committee

Of Lehigh University

In Candidacy for the Degree of

Master of Science

In

Polymer Science and Engineering

Lehigh University

May 2016

CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the Master of Science in Polymer Science and Engineering.

_____
Date

_____
Thesis Advisor
Raymond A. Pearson

_____
Chairperson of Department
Helen M. Chan

Acknowledgements

Many people were involved in the completion of the work, directly and indirectly. I would like to thank Dr. Raymond Pearson and the distance education department for all the help and guidance they provided over the course of pursuing a Masters. I would also like to thank Sue Getts and Bill Zanelatto, my managers at Testors and Seymour that supported me in this endevour and allowing for this great opportunity. A special thanks goes to Stephen Sawar who encouraged me to go for a Masters while my colleauge at Testors and then supporting me through the final stages as my recent supervisor at Seymour.

Lastly, but far from least, my eternal gratitude for my loving and amazing wife, Kristen. I never would have made it without her unending support.

Table of Contents

List of Tables

List of Figures

Abstract

Latex coatings have made large bounds in their development and have become a staple in architectural and decorative paints. Recent years have seen large growth in industrial and automotive coatings as well. However, one area that has not seen the same growth is aerosol coatings. While there are many consumer products that use latex resins, many latex resins do not product an acceptable coating from an aerosol.

This study investigated many latex resins for their performance as an aerosol coating. The properties of the latex resins were examined for those that became a successful coating and those that did not. Latex properties such as resin type, pH, percent solids, and glass transition temperature were compared. Additionally, the influence of the total coating formulation was also explored. It was found that a far greater amount of resins created from condensation polymers made successful coatings as compared to resins created from addition polymers. Other properties of the latex resins had less correlation to success or failure. Overall, the data suggested that the primary influence of a latex resin's chances of success as an aerosol coating lies within the makeup of the resin polymer itself.

1. Introduction:

Coatings have been used to protect and beautify structures for centuries. Traditional solvent based coatings however present a significant hazard to health and environment. With the advent of latex coatings, a safer and more environmentally friendly option was made available. Although there are many water-borne aerosol products used today, for example hair sprays, household cleaners, and room fresheners, not much progress have been made making a water-borne aerosol coating. Although there have been a number of patents filed for water-borne aerosol coatings, a visit to a local paint retailer will find them generally missing from the shelves.[1,2,3] There are many difficulties with water-borne coatings, for instance keeping the latex emulsion stable for a reasonable shelf life or producing a smooth, clean film for decorative or industrial use, that are difficult to overcome in aerosol form. This work set out to further understand what makes a latex resin a good candidate for being used in an aerosol coating.

1.1. Latex Coatings:

Coatings are comprised of three basic components: binder, pigment, and solvent.[4] Additives such as dispersants, surface active agents (surfactants), and defoamers are commonly used in a paint formulation as well. Water-borne coatings in particular usually also have coalescing solvents, thickeners, a pH adjuster, and/or a biocide.[5] The solvent serves as a carrier of the binder and pigment to the desired substrate. After application, the solvent evaporates allowing the binder to thicken, adhering the pigment and substrate. This is the function of a paint in its most simplest of terms.

The defining facet of a latex or water-borne coating is that water is used as the primary solvent. Because most coating resins are not soluble in water, emulsion polymerization is used to create polymer latexes for use in coatings. The basis of emulsion polymerization techniques utilized today trace back to the 1940's.[6,7,8] Emulsion polymerization today still follows the same basic structure: with the aid of a surfactant, emulsify a mixture of water and monomer, then add an (usually water soluble) initiator and let "cook."[9] The resulting polymer emulsion is now the latex coating resin.

The color of a coating comes from its pigments, but they can also add other functions as well. Pigments can be either organic or inorganic: copper phthalocyanine (blue and green) and titanium dioxide (white) are examples of each type, respectively. Extender pigments, like calcium carbonate, can be used to mechanically strengthen the coating film but add little strength of color. Lastly, there are also functional pigments, for instance, zinc phosphate is commonly used to improve the corrosion resistance of a coating over steel.[10] A coating may be formulated without pigment, which results in a "clear coat." The formulations of this study were all without pigment.

Dispersant additives are commonly used in conjunction with pigments. There function is to first aid in the exfoliation of the pigment particles, then adsorb onto the pigment surface. The dispersants then continue to inhibit agglomeration of the pigment particles though electrostatic repulsion and/or steric hindrance.[11]

A surfactant can be added to a paint formulation to reduce the surface tension of the paint. Reducing the surface tension allows the paint to better wet the substrate it is applied to. If the surface tension of the paint is too high it will not flow out onto a substrate. The

surfactant also serves to reduce surface tension gradients that can arise during the solvent evaporation from the applied film which in turn can lead to surface film defects like orange peel or picture framing.[12] With the high surface tension of water, a surfactant is almost always required for proper application. As a note, the surfactants used for this purpose are separate from the surfactants used during the emulsion polymerization of the resin.

A common defect encountered in coatings is foam. It is created when air is mixed into the paint concentrate, either during processing or application. With aerosols, foam can also be formed by residual propellant leaving the concentrate shortly after application to the substrate. Water-borne coatings are generally more susceptible to foam generation, and as has been found in the art, it can be expected for water-borne aerosols to generate foam. A defoamer additive can be added to a paint formulation to alleviate foam. The principal attribute of a defoamer is that is has a degree of incompatibility with the coating solution which serves as centers for bubble collapse to start.[13] This causes the air micelles (foam bubbles) to destabilize, leading to the foam breaking quickly – specifically such that the foam breaks before the viscosity of the applied film rises too high (from solvent evaporation) for adequate flow to fill in the space left by the popped foam bubble.

The mechanism of latex film formation happens over three stages.[14] First, as the water evaporates, the dispersed resin particles begin to close together. Second, once the water has left the particles pack together and become deformed against one another. Lastly, the compacted particles coalesce to form a continuous film. Each latex resin has a property known as the minimum film formation temperature (MFFT), this is the minimum temperature the resin must be at for stage three to occur.[15] For a coating to form a film

when the ambient temperature is below the MFFT of the base resin, a coalescing solvent, or coalescent, must be added to the formulation. The coalescent acts to lower the MFFT of the coating. Acrylic resins for coatings commonly have a MFFT above room temperature and require a coalescent when used in a coating. Glycol ethers are commonly used coalescents.

The rheology profile of a paint is important for the proper application of the coating. This means a paint should be shear thinning, so that it will flow easily as it is being applied then thicken once it is on the substrate so as to not run. Shear thinning is doubly important for aerosol delivery as a lower viscosity will provide a more uniform atomization of the coating.[16] Rheology control additives, or thickeners, can be added to give the coating concentrate a thixotropic nature. Unlike solvent-borne resin solutions, resin latexes generally have a low viscosity and require one or more thickeners in the formulation to create a coating with a tailored rheology profile. Some examples of thickeners include, hydroxyethyl cellulose, alkali swell able emulsions, and hydrophobically modified polyurethanes.

Stability of a latex resin can be pH dependent. Latex resins used in coatings generally require a basic pH. This is advantageous for aerosol use, since most aerosol cans for coatings (explained further below) are made from tinplate steel, which is less susceptible to corrosion the higher the pH. The two most common additives for controlling pH in coatings is ammonia and 95% amino-methyl pyrrolidone (AMP-95).

Lastly, some resins used in water-borne coatings are susceptible to bacterial or fungal attack. For these resins a biocide can be added to the formulation.

1.2. Aerosol Coatings:

Modern aerosol paints can be considered as first being invented about 65 years ago.[17] Since that time the components of an aerosol coating have changed little. The primary components consist of the coating concentrate, propellant, can, valve (with diptube for upright usage), actuator, and in-can agitator. Figure 1-1 shows a modern aerosol paint can next to a 1950's aerosol paint can made under patent US2580132 A. Although there has been substantial advancement in aerosol technology since then, the basic design has changed little.

Figure 1-1. Modern aerosol paint can on the left next to an aerosol paint can from the 1950's.

1.2.1. Can Components

The container for aerosols can be made from steel, tinplated steel, aluminum, plastic, or glass. The most common used in the US is tinplate steel due to it being economical, having increased resistance to corrosion than plain steel, and being capable of safely withstanding common aerosol pressures.[18] Steel is generally not used for aerosol coatings with plastic and aluminum utilized only for specialty use. Glass container are often used for laboratory work during aerosol formulation development, commonly known as a Fisher-Porter bottle.

The valve and actuator can be considered the working parts of an aerosol. They function as the on/off switch, control the flow rate of dispensing, and influence the atomization profile. The size and shape of the actuator orifice controls the shape and size of the spray profile. For coatings, this will be a round orifice to create a cone spray or a rectangular orifice to create a fan spray. The internal portion of an actuator is generally a direct, open path, though some include channels for the product to pass through which aids atomization.[19] Male actuators contain a stem for insertion into a female valve. The end of the stem will have a slot cut out of it which allows product to flow into it from the valve.

The primary components of a valve are the valve body, spring, gasket, and diptube; male valves will also have a stem. The body houses the spring and gasket, and is what the actuator attaches to. Many valve bodies have a small hole (generally 200 – 400 μm) in the base called a vapor tap. The vapor tap allows a small amount of the gas phase propellant to escape with the liquid product. Expansion of the pressurized gas as it leaves the actuator aids atomization of the coating.[20] The spring serves to push the male actuator stem or male valve

stem back to the closed position when the actuator is no longer depressed. Similar to a male actuator stem, a male valve stem will have a hole near its base that allows product to flow from the valve, into the stem, and to the actuator. The gasket serves to seal the slot or hole in the stem, preventing flow. When the actuator is depressed, the gasket deforms revealing the stem slot or hole allowing product to flow.[21] Valve gaskets for aerosol coatings are generally made from either nitrile rubber or neoprene. A depiction of the aerosol component function is shown in Figure1-2.

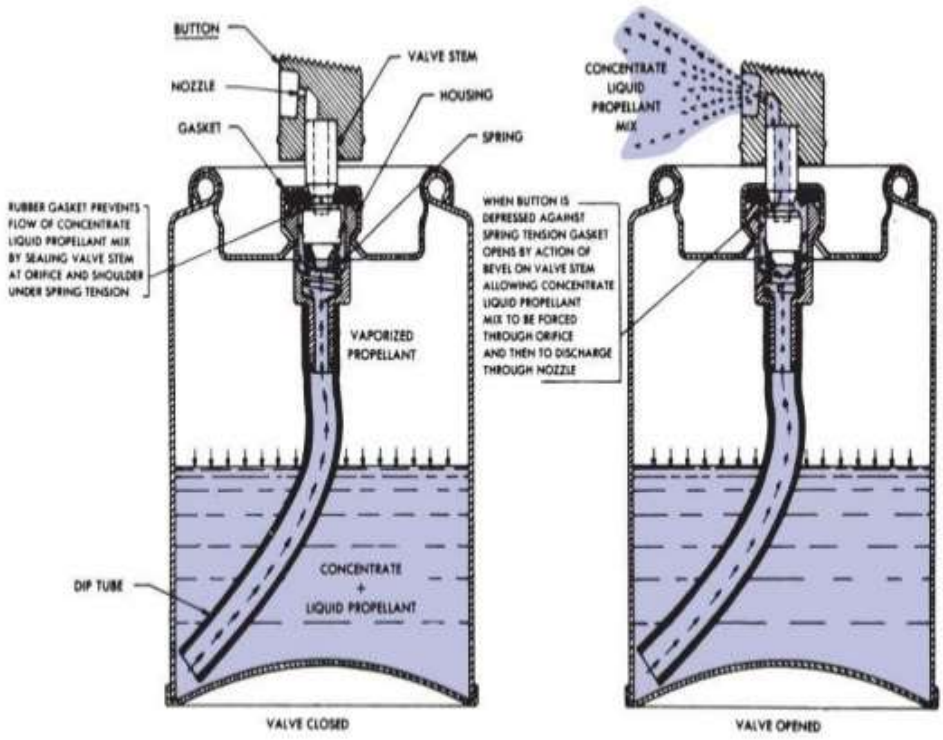

Figure 1-2. Schematic depiction of the function of an aerosol can.[22]

1.2.2. Propellant

Propellant is what makes an aerosol an aerosol. It is what generates the pressure to expel the product from the can. There are two types of propellants used in aerosols, compressed gas or liquefied gas. With the exception of specialty products, aerosol coatings use liquefied gas propellant that provides the advantage of a consistent discharge profile over the full volume of the product. This is because the pressure exerted by a liquefied gas is governed by Raoult's law that states the vapor pressure of a mixture is the weighted sum of the vapor pressures of each component. With the liquefied gas a part of the solvent solution of the paint concentrate, the vapor pressure of the liquid – and therefore the pressure within the aerosol can – remains constant throughout the discharging of the can.

Modern aerosol coatings primarily utilize hydrocarbon propellant, which will be a blend of propane, iso-butane, and/or n-butane. The blends are made to give a particular vapor pressure, for example, a 32/68 (w/w) blend of liquid propane/isobutane will have a vapor pressure of 86 psia (~593kPa) at 26 °C.[23] Hydrocarbon propellant use with coatings have the advantages of being low cost, adequate solubility with organic solvents, and within a pressure range that gives desirable performance. In terms of use with a water-borne coating however, lower alkanes have very low solubility in water.[24]

A liquefied gas propellant that has better promise for use with water-borne coatings is dimethyl ether (DME). The vapor pressure of DME is desirable for aerosol use, 87 psia (~600 kPa) at 26 °C.[25] It is partially miscible with water having a miscibility window of up to 34.1% (w/w) DME and greater than 94.1% (w/w) DME.[26] DME/water mixtures can be easily cosolved with a lower alcohol. A ternary diagram of DME/water/ethanol is shown in

Figure 1-3. As can be seen in the diagram, 6.5% (m/m) of ethanol is enough to make DME and water miscible at all concentrations. Goumin, et.al. also note that methanol and isopropanol have the same common solvent factor for DME/water as ethanol.

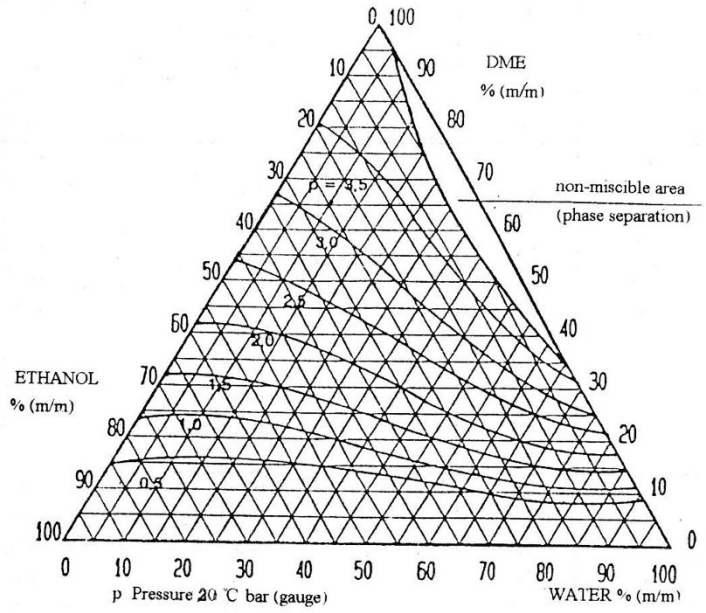

Figure 1-3. Ternary diagram of DME-water-ethanol.

2. Experimental:

The approach of this study was conducted in two stages. The first stage was concerned primarily with the comparing the viability of different polymer types used in a latex coating aerosol. Many commercially available latex resins were tested in this stage. The second stage explored the effect of co-solvents on the success of a latex coating in an

aerosol. Only a subset of the resins from stage I was chosen for use in stage II. Resins were chosen to provide a variety of polymer types and success or failure in stage one. Availability of adequate resin quantity also limited the selection for stage two. The resins used in this study are listed in Tables 2-1 through 2-6.

Table 2-1: Acrylic Resins

Acronal DS 2159	BASF
Aquamac 510	Polynt
Carboset CR-785	Lubrizol
Encor 651	Arkema
Encor DT 100	Arkema
Encor DT 211	Arkema
Encor Flex 187	Arkema
EPS 2705	Engineered Polymer Solutions
EPS 2717	Engineered Polymer Solutions
Fastrack 2706	Dow
Fastrack 3427	Dow
Fastrack HD-21A	Dow
Fastrack XRS	Dow
Joncryl PRO 1524	BASF
Joncryl PRO 1537	BASF
PD-0449	H.B. Fuller
PD-3900	H.B. Fuller
Pliotec CR78	Omnova
Rhoplex WL-96	Dow
Rovene 6117	Mallard Creek
Synthemul 40413-03	Reichhold
Ucecryl B 1009	Allnex

Table 2-2: Styrene Acrylic Resins

AC-219	Picassian
AC-295	Picassian
Aquamac 260	Polynt
Aquamac 700	Polynt
Aquamac 705	Polynt
Aquamac 740	Polynt
Arolon 820-W-49	Reichhold
AS 2685	Alberdingk Boley
Encor 123	Arkema
Encor DT 250	Arkema
Encor DT 400	Arkema
EPS 2535	Engineered Polymer Solutions
Orgal CX 3011	Organic Kimya
Orgal CX 3060	Organic Kimya
PD-0600	H.B. Fuller
Pliotec HDT 12	Omnova
RayKote 1515	Specialty Polymers
Revacryl AE 6030	Synthomer
Rovene 6087	Mallard Creeek
Rovene 6131	Mallard Creek
Texicryl 13-061	Scott Bader
Texicryl 13-065	Scott Bader
Ucecryl B 3025	Allnex

Table 2-3: Self-cross Linking Acrylic Resins

Avanse 200	Dow
Carboset CA-600	Lubrizol
EPS 2291	Engineered Polymer Solutions
NeoCar 850	Arkema
NeoCryl A-1127	DSM
P-2893	Dura Pro
R5181	Essential Polymers
R5194	Essential Polymers
RayCryl 1859	Specialty Polymers
RayFlex 777	Specialty Polymers
Viacryl VSC 6295w	Allnex

Table 2-4: Alkyd Resins

Beckosol AQ 210*	Reichhold
Beckosol AQ 400*	Reichhold
Beckosol AQ 510*	Reichhold
Resydrol AY 6150w*	Allnex
Synaqua 821-1377*	Arkema
Uradil AZ 760*	DSM
Urotuf F600*	Reichhold

*Oxidative cure resin

Table 2-5: Urethane Resins

Aquence PI QW26	Henkel
Bayhydrol UH 2342	Bayer Material Science
Bayhydrol UH 2593/1	Bayer Material Science
Bayhydrol UH XP 2592	Bayer Material Science
Daotan TW 1252	Allnex
Daotan VTW 6462*	Allnex
EPS 4203	Engineered Polymer Solutions
Eterane 89334	Eternal
NeoRez R-972	DSM
PR-1238	Quaker Color
PR-1378	Quaker Color
PR-1470	Quaker Color
R4565	Essential Polymers
Unithane IC-505	Union Specialties
Unithane IC-807 SF	Union Specialties
Unithane IC-953 CP	Union Specialties

*Oxidative cure resin

Table 2-6: Other Resins

Elvace 756	H. B. Fuller	(Vinylacetate-ethylene)
Encor 182	Arkema	(Vinylacetate-ethylene)
Encor 282	Arkema	(Vinylacetate-ethylene)
Epitex 611S*	Arkema	(Epoxy-ester)
LA-8569*	US Polymers	(Acrylic/Epoxy-ester)
P-4222	Dura Pro	(Vinyl/Acrylic)
RayPlus 1097	Specialty Polymers	(Acrylic/Al_2O_3 core-shell)
RS-3120	Butvar	(Vinylbutyrate)
Synthemul 40136-00	Reichhold	(Vinyl/Acrylic)

*Oxidative cure resin

2.1. Formulations:

As outlined above, there are many components that can go into a latex coating. Generally a coating formulation would be optimized to a particular resin and end use performance. Developing a separate, optimized formula for each resin tested would have been prohibitive by both time and material quantities. For stage I of this study the formula was selected such that it would reasonably expect to achieve adequate film formation for characterization within the scope of this study for many latex resins. The stage II formulations were chosen in a similar fashion. All of the formulations are explained in further detail below. All materials were used as received.

2.1.1. Stage I:

Many latex resins, particularly acrylics, have a MFFT greater than room temperature (~20° C) and therefore require the addition of a coalescent for proper film formation. The coalescents used in stage I were dipropylene glycol methyl ether (DPM, Univar) and Eastman Texanol™ Easter Alcohol (Texanol, Nexeo). These two solvents were chosen as the coalescents so as to have one water miscible and one water immiscible, DPM and Texanol, respectively. The coalescent level was held constant to the total formula to have a constant ratio of cosolvent to DME (Air Products) throughout stage I. This equates to approximately 20phr coalescent for a 35% solids latex resin. As a note, it is common in the art that when two coalescing solvents are used in a latex formulation for the one with the faster evaporation rate to be used in a greater amount.

Air entrapment is a common occurrence with spray applied coating, particularly with aerosols. To ensure (or at least improve) air release from the coating film, BYK-24 (BYK), a

silicone defoamer, was included. Additionally, with water having a high surface tension, BYK-333 (BYK), a silicone surfactant, was added to promote proper wetting of the substrate for better film formation.

For rheology control, Rheolate 288 (Elementis) was used. It is a polyether polyurethane type associative thickener designed for spray application. Because the thickening efficiency varies per individual resin, the amount to add was determine at the time of addition. Rheolate 288 was added until the paint concentrate was visually deemed to be at an acceptable viscosity for proper aerosol application or until an addition level of approximately 2-2.5% was reached, which ever came first. This limit was imposed to maintain comparable addition levels among all of the resins tested.

Corrosion of the aerosol can is a concern with any aqueous formula. 95% aqueous solution of 2-amino-2-methyl-1-proanol (AMP-95, Nexeo) is added to maintain a basic pH which, while necessary for most latex resin also inhibits corrosion inside the aerosol can. A pH of around 9 is generally sought in the art.

For the resins that require an oxidative cure, OXY-Coat 1101 (OM Group) was added at 1 phr. It is an iron based catalyst for the curing mechanism – also known as a drier in the art. To prevent premature curing of the resin, a fugitive inhibitor is also added. Ascinin 0445 (OM Group) was used in this study. The full formulation for stage I is shown in Table 2-7.

Table 2-7: Stage I Formulation

Resin	260g
Water	130g
DPM	12g
Texanol	6g
BYK-24	1g
BYK-333	0.8g
AMP-95	1.6g
Rheolate 288	*
OXY-Coat 1101**	1 phr
Ascinin 0445**	1.2g

*Amount of Rheolate 288 was determined at time of addition by thickening efficiency
**Only used with oxidative cure resins

2.1.2. Stage II:

Stage II explored the effect of the solvent matrix on the viability of the use of a latex resin in an aerosol. The variations tested were two different levels of water to latex ratios, using only water miscible coalescents, using only water immiscible coalescents, and adding alcohol to encourage increased water/DME miscibility. The resins tested in Stage II are listed in Table 2-8.

Table 2-8: Stage II Resins

Aquamac 700	Polynt	(Styrene Acrylic)
Bayhydrol UH 2593/1	Bayer Material Science	(Urethane)
Carboset CR-785	Lubrizol	(Acrylic)
EPS 4203	Engineered Polymer Solutions	(Urethane)
NeoCar 850	Arkema	(SXL Acrylic)
P-4222	Dura Pro	(Vinyl/Acrylic)
Rovene 6131	Mallard Creek	(Styrene Acrylic)
Synaqua 821-1377*	Arkema	(Alkyd)

*Oxidative cure resin

The first variable tested in stage II was the amount of water in the formula. In stage I water was added at one half the amount of latex resin. For stage II one trial set the amount of water equal to that of latex resin, and a second trial set the amount of water to double the latex resin. The total amount of water plus latex resin was kept constant with stage one. This corresponds to formulas II.a and II.b in Table 2-9, respectively.

Next tested in stage II was the influence of coalescing solvents. Two sets of coalescing solvents were chosen, one set with both being fully miscible with water and the other set with both having low water miscibility. The water miscible set consisted of ethylene glycol n-butyl ether (EB, Brenntag) and diethylene glycol n-butyl ether (DB, Emco). The low water miscibility set consisted of propylene glycol n-butyl ether (PNB, Emco) and dipropylene glycol n-butyl ether (DPNB, Emco). These are formulas II.c and II.d in Table 2.9, respectively. EB/DB and PNB/DPNB were chosen because they are commonly used together in the art.

Lastly, stage II tested the effect of the addition of alcohol. As was shown above, ethanol addition to a water-DME mixture will make it miscible at all ratio amounts. However, the coatings industry commonly uses denatured ethanol rather than 200 proof (or 190 proof for that matter), therefore using neat ethanol for this study would have reduced significance to industrial application. Because of this, methanol (Brenntag) was chosen as shown in formula II.e in Table 2-9. The amount of methanol utilized in formula II.e is such that it equates to approximately 10% methanol on water/DME in the lower fill ratio and approximately 8% methanol on water/DME in the higher fill ratio.

Table 2-9: Stage II Formulations

II.a	
Resin	195g
Water	195g
DPM	9g
Texanol	4.5g
BYK-24	1g
BYK-333	0.8g
AMP-95	1.6g
Rheolate 288	*
OXY-Coat 1101**	1 phr
Ascinin 0445**	1.2g

II.b	
Resin	130g
Water	260g
DPM	6g
Texanol	3g
BYK-24	1g
BYK-333	0.8g
AMP-95	1.6g
Rheolate 288	*
OXY-Coat 1101**	1 phr
Ascinin 0445**	1.2g

II.c	
Resin	260g
Water	130g
EB	12g
DB	6g
BYK-24	1g
BYK-333	0.8g
AMP-95	1.6g
Rheolate 288	*
OXY-Coat 1101**	1 phr
Ascinin 0445**	1.2g

II.d	
Resin	260g
Water	130g
PNB	12g
DPNB	6g
BYK-24	1g
BYK-333	0.8g
AMP-95	1.6g
Rheolate 288	*
OXY-Coat 1101**	1 phr
Ascinin 0445**	1.2g

II.e	
Resin	260g
Water	130g
DPM	12g
Texanol	6g
Methanol	49g
BYK-24	1.1g
BYK-333	0.9g
AMP-95	1.8g
Rheolate 288	*
OXY-Coat 1101**	1 phr
Ascinin 0445**	1.2g

*Amount of Rheolate 288 was determined at time of addition by thickening efficiency
**Only used with oxidative cure resins

2.1.3. Aerosol make up

This study used a standard aerosol coating configuration. The aerosol can (B-Way) was a tin-plated 202x406 can, commonly referred in the art as a 6 fl oz can. The valve (Aptar) was a standard female value with a stainless steel spring, buna gasket, and .008 vapor tap. The actuator (Aptar) was a MARC-18-2027 with a .020 orifice and with mechanical break up. A 5/8" glass marble (Jabo, Inc) as added to each can as the agitator. The concentrates were kept in a glass jar (The Cary Company) with a PTFE lined lid during aging at 49°C.

The fill ratio of coating concentrate to propellant was tested at two different levels. The first was 75% concentrate and 25% DME (w/w) and the second was 60% concentrate and 40% DME (w/w). All aerosol cans were filled to a total weight (concentrate plus DME) of 140g. Laboratory filling of propellant is generally done volumetrically, therefore this equated to 105g concentrate/52.5mL DME for the 75/25 fill ratio and 84g concentrate/84mL DME for the 60/40 fill ratio.

2.2. Characterization:

The primary criteria for the success or failure of a resin in an aerosol coating will be visual inspection of the applied dried film. All samples, concentrate and aerosol cans, were allowed to sit at room temperature (~21°C) for one to four days before initial testing to allow for complete equilibrium between concentrate and DME. After initial testing, samples were placed in an oven set at 49°C for aging at elevated temperature for four weeks. Any sample that was deemed failed (outlined below) at the initial testing was discontinued from the aging testing.

All spray outs and drawdowns were done on 2DX Leneta cards. Aerosols were sprayed to an approximately 4-6 mil wet film thickness and hung vertically to dry. Concentrate samples were applied using a 3 mil bar film applicator and laid flat to dry. After the initial drying period of 1-3 hours, all cards were transferred to upright drying racks. The films were allowed to further dry – or cure as is the case for the resins with oxidative curing – for at least 3 days before reading the gloss and performing the visual assessment. Gloss measurements were conducted using a Gardner Micro-TRI-Gloss gloss meter. An image of the bar film applicator and gloss meter are shown in Figure 2-1.

Figure 2-1. Left: bar film applicator with Leneta card on a vacuum plate. Right: Micro-TRI-Gloss gloss meter.

To ensure that any change seen in the aerosol samples after the elevated temperature aging were influenced by the DME, the concentrate was also tested by measuring pH and viscosity before and after aging. pH was measured using a Eutech Instruments pHTestr10 pH meter and viscosity was measured using a Brookfield RVDV-I+ viscometer. Spindle size and rpm of viscosity measurement was determined at initial testing for the most optimal combination for the specific concentrate. For post aging testing when the viscosity had significantly changed, viscosity measurement was performed at the same rpm setting whenever possible within the physical size limitations imposed by the jar size. Images of the viscometer and pH meter are shown in Figure 2-2.

Figure 2-2. Left: Brookfield RVDV-I+ viscometer shown with a #3 spindle. Right: Eutech Instruments pHTestr10 hand held pH meter.

When evaluating the visual appearance of the water borne aerosol coatings, particular defects are looked for. The defects include seeding, kick out, dry spray, snotty clumps, and webby or stringy spray. Examples of each of these are shown in Figure 2-3. Also encountered in this study was heterogeneous separation of the concentrate after aging, which

will be discussed in the results section below. An example of the resulting film from this separation, as well as an example of a desired film is shown in Figure 2-4.

Figure 2-3. Examples of spray outs from failed formulations. a) dry spray, b) kick out, c) seeds, d) snotty spray, e) stringy spray, f) webby spray.

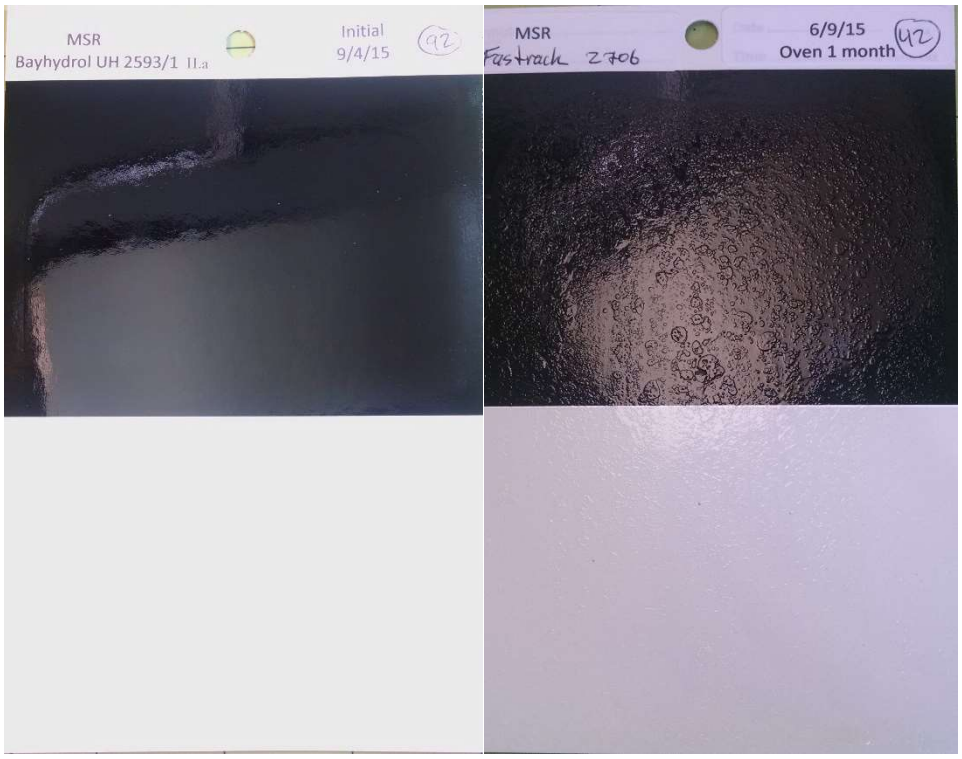

Figure 2-4. Left: Example of a desired/passing draw down – clean, clear, and glossy. The same criteria is also applied to the aerosol spray outs. Right: Example of a draw down from a concentrate that had heterogeneous separation during aging.

3. Results and Discussion

Each of the resins a part of this study were made into paint concentrates according the formulation(s) described above. Aerosols from these concentrates were sprayed and evaluated both after the initial makeup of the aerosol and after aging for thirty days at 49 °C. Each resin, at each of the two concentrate/propellant fill ratios, where given one of three ratings: pass, initial, or fail. To receive a pass rating, the applied coating had to be clear, glossy, and free of defects as described in section 2 for both the initial spray out and after the

elevated temperature aging. A fail rating was given when the initial spray out contained any of the defects described in section 2. A rating of initial was given when the initial spray out was a pass, but failed after aging.

3.1. Stage I

For stage I eighty-eight different resins were tested. About half of the formulations received a failing rating, with the remainder split between ratings of pass or initial. The ratings for each of the resins and fill ratios are shown in table 3-1. It can be seen that the amount of DME has an effect on the success of a coating. Many of the resins tested received a pass at a 75/25 fill ratio, but failed at 60/40. This strongly suggest that DME is a primary factor in the stability of the resin.

Other various trends were also examined among the base resins and the formulated concentrates, including resin type, %°solids, latex particle size, glass transition temperature (T_g) and MFFT of the resin, pH of the resin latex and of the concentrate, and viscosity change of the concentrate upon aging. These trends will be discussed below.

Table 3-1. Stage I pass/fail results for all resins.

Resin	75/25	60/40	Resin	75/25	60/40
Acronal DS 2159	F	F	NeoCar 850	F	F
Aquamac 260	I	I	NeoCryl A-1127	F	F
Aquamac 510	F	F	NeoRez R-972	P	P
Aquamac 700	I	F	Orgal CX 3011	P	F
Aquamac 705	F	F	Orgal CX 3060	P	F
Aquamac 740	I	F	P-2893	P	P
Aquence PI QW26	P	P	P-4222	F	F
Arolon 820-W-49	I	I	PD-0449	F	F
AS 2685	P	I	PD-0600	F	F
Avanse 200	F	F	PD-3900	F	F
Bayhydrol UH 2342	P	F	Picassian AC-219	I	F
Bayhydrol UH XP 2592	P	P	Picassian AC-295	F	F
Bayhydrol UH-2593/1	P	P	Pliotec CR78	F	F
Beckosol AQ 210	I	I	Pliotec HDT 12	P	I
Beckosol AQ 400	I	I	PR-1238	F	F
Beckosol AQ 510	P	P	PR-1378	F	F
Carboset CA-600	I	F	PR-1470	I	F
Carboset CR-785	F	F	R4565	I	F
Daotan TW 1252	P	P	R5181	I	I
Daotan VTW 6462	P	P	R5194	P	I
Elvace 756	F	F	RayCryl 1859	F	F
Encor 123	F	F	RayFlex 777	F	I
Encor 182	F	F	RayKote 1515	F	F
Encor 282	I	F	RayPlus 1097	F	F
Encor 651	F	F	Resydrol AY 6150w	P	P
Encor DT 100	F	F	Revacryl AE 6030	P	F
Encor DT 211	F	F	Rhoplex WL-96	F	F
Encor DT 250	F	F	Rovene 6087	I	F
Encor DT 400	F	F	Rovene 6117	P	F
Encor Flex 187	F	F	Rovene 6131	P	F
Epitex 611S	P	P	RS-3120	F	F
EPS 2291	P	I	Synaqua 821-1377	P	P
EPS 2535	F	F	Synthemul 40136-00	I	F
EPS 2705	P	F	Synthemul 40412-03	P	P
EPS 2717	P	F	Texicryl 13-061	P	F
EPS 4203	P	F	Texicryl 13-065	F	F
Eterane 89334	I	F	Ucecryl B 1009	F	F
Fastrack 2706	F	F	Ucecryl B 3025	I	F
Fastrack 3427	I	P	Unithane IC-505	P	F
Fastrack HD-21A	I	I	Unithane IC-807 SF	P	F
Fastrack XRS	I	F	Unithane IC-953 CP	P	F
Joncryl PRO 1524	I	I	Uradil AZ 760	I	I
Joncryl PRO 1537	P	F	Urotuf F600	I	P
LA-8569	P	P	Viacryl VSC 6295w	P	F

P = passed aging. I = passed initial, failed aging. F = failed initial.

3.1.1. Effect of Resin Type

The rating totals separated by resin type are shown in Figure 3-1. It can be easily seen that there is a difference between the condensation polymers (urethane, alkyd, and epoxy-ester) and the addition polymers (acrylics and vinyls). Even though the majority of the sampled resins are addition polymers, more condensation polymers received a pass rating. It is clear that condensation polymers have a greater probability for success in an aerosol coating.

One possible explanation could be the structure of the polymer backbone. Acrylic and vinyl polymers generally have an ethylene backbone as opposed to the ester and urethane linkages of the condensation polymers. With DME being an oxygenated compound, assuming some portion of the DME enters the polymer particles, it could have better compatibility with the oxygenated polymer backbones and less prone to destabilize the resin particles.

Another explanation for this trend is chain length or average molecular weight. For commercial resins molecular weight information is often not available, however it is generally found that addition polymers for coating resins on average will have higher molecular weights that condensation polymers for coating resins, and especially so for oxidative cure resins. The shorter chain lengths of the condensation polymers may contribute to their higher stability in DME.

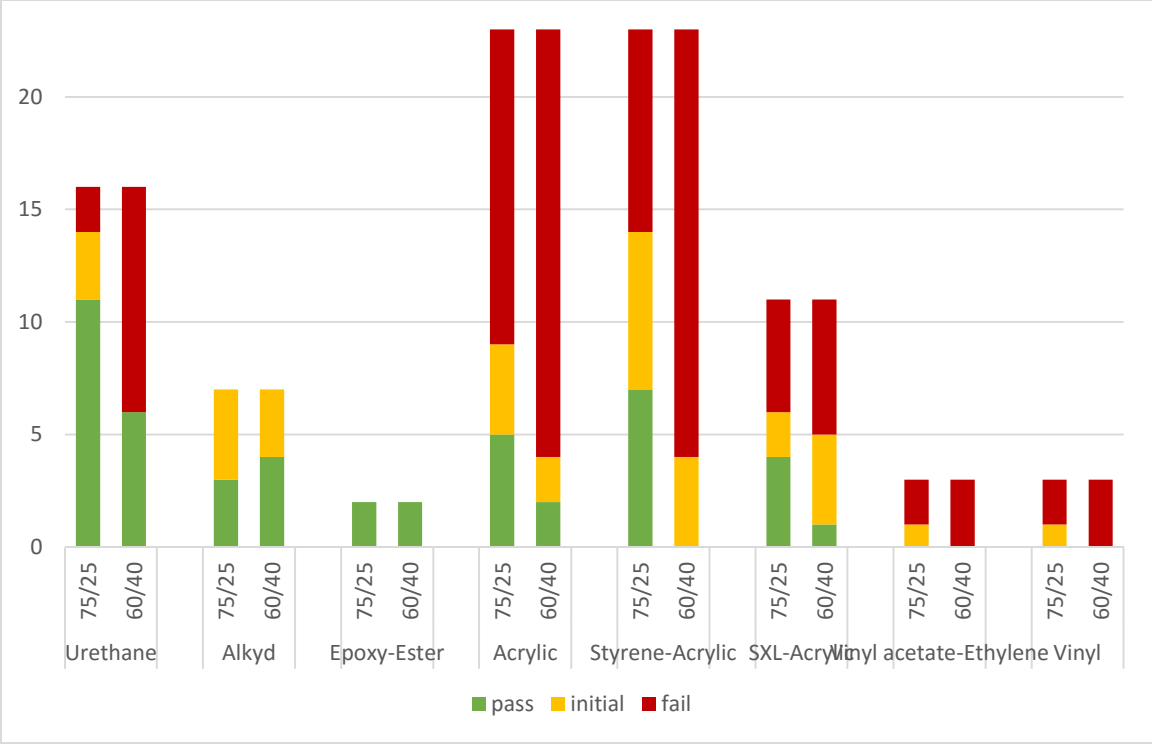

Figure 3-1. Ratings by resin type.

3.1.2. Effect of Resin Solids

Each of the aerosols were sorted by the weight percent solids of the latex resin, shown in Figure 3-2. As the resin solids goes down, the proportion of passing resins increases. The correlation, however, is not that strong. The 40% - 49% and 50% - 59% groups are quite similar and the 30% - 39% group only has about one half the amount of samples. There are suggestions of an influence by weight % solids, but that cannot be said conclusively.

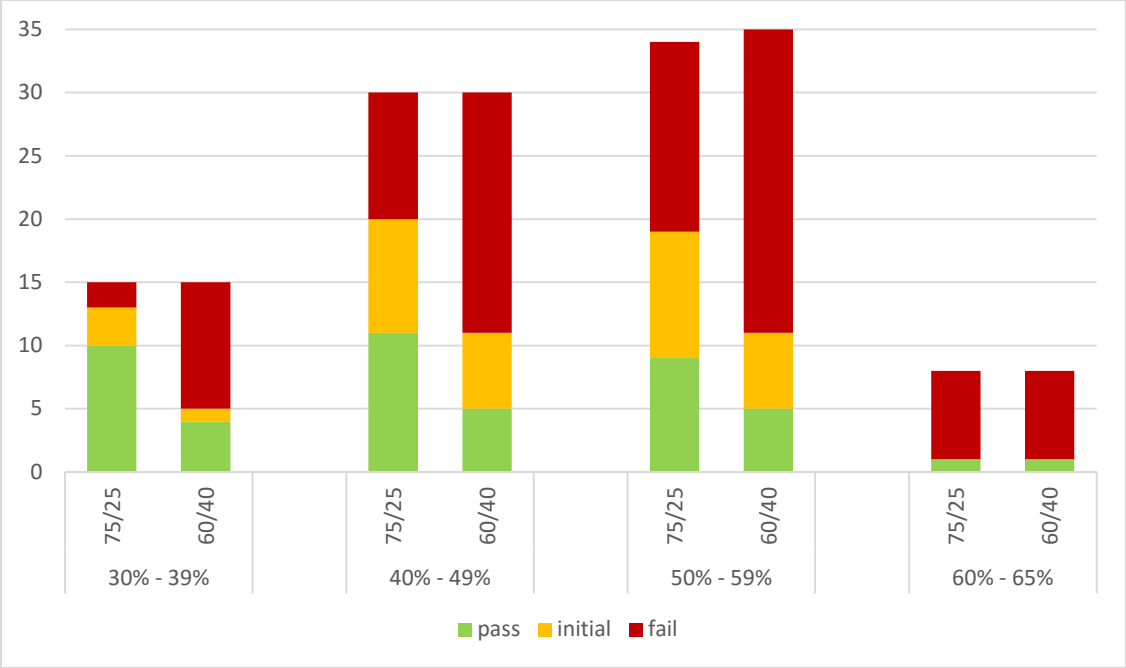

Figure 3-2. Ratings by latex resin weight % solids.

Section 3.1.1 showed a difference between condensation and addition polymers. All except one of the resins in the 30% - 39% group were condensation polymers which can account for the higher percentage of passing resins. The weight % solids data with the condensation and addition polymers separated is presented in Figure 3-3. The only group to have no passing resins is the high solids (60% - 69% group) addition polymers. With very little difference between the 40% -49% and 50% -59% groups, it suggest only a minor dependence on weight percent solids if any.

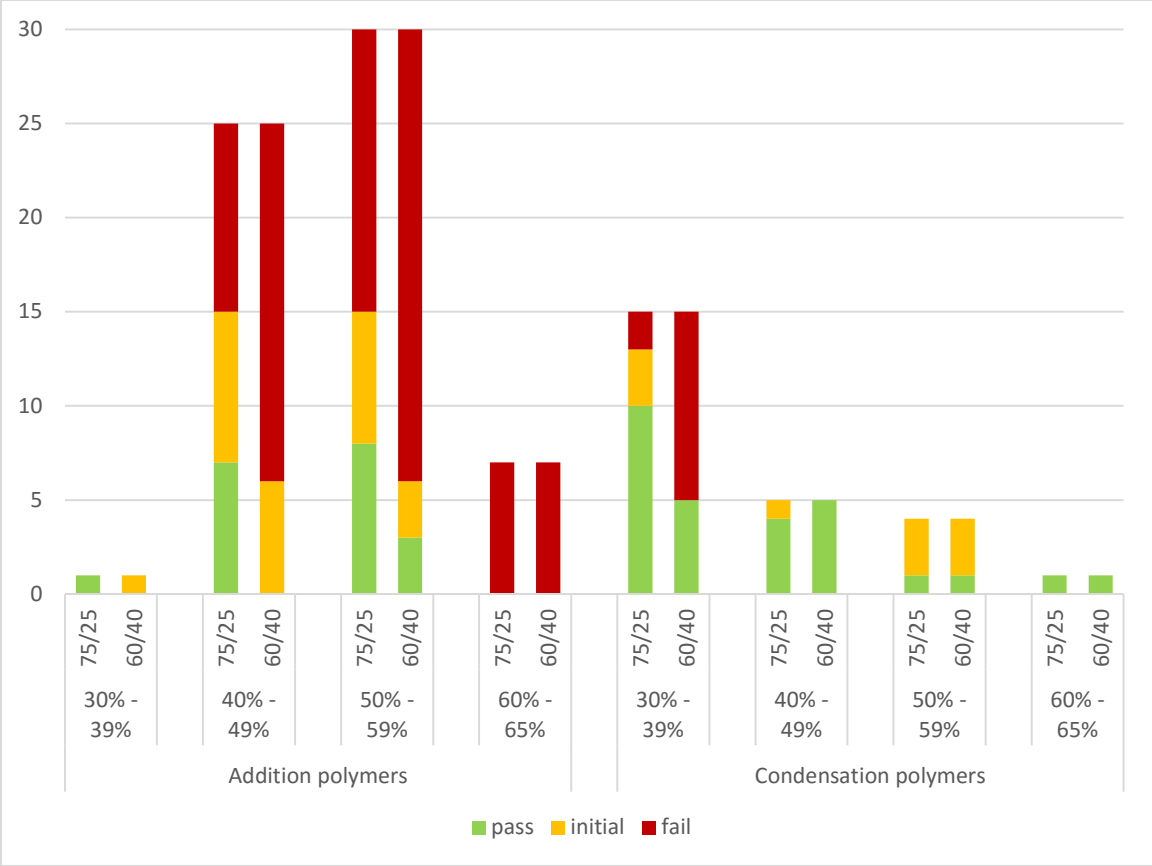

Figure 3-3. Ratings by latex resin weight % solids; addition and condensation polymers.

3.1.3. Effect of Resin Particle Size

Thirty-one of the addition polymer resins had disclosed their latex particle size. Only four of the condensation polymer resins disclosed particle size, therefore their inclusion in this section was determined to unnecessarily confound the results and were excluded. The ratings results for those resins are shown in Figure 3-4. The data does not show any significant trend for particle size and aerosol stability.

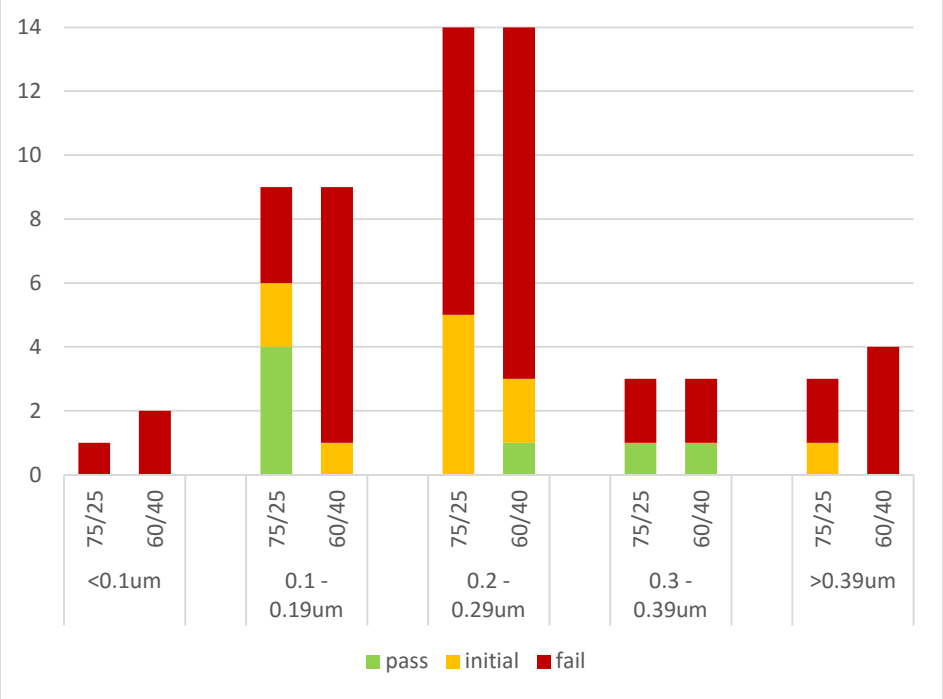

Figure 3-4. Ratings by latex particle size, addition polymers.

3.1.4. Effect of Glass Transition Temperature

Many of the acrylic resins divulged their glass transition temperature. The results of these resins grouped by T_g are shown in Figure 3-5. With the exception of two outliers, all of the acrylic resins with a passing rating have a T_g between 10 °C and 39 °C. This suggest that T_g could be related to success in an aerosol. Although the contributing factor cannot be determined directly from this data, it does encourage further investigation. The T_g of a resin is primarily controlled by the monomer selection, but can be adjusted with additives like a plasticizer. Because of this, speculation into what monomers may be responsible for compatibility with DME will require a more in-depth study.

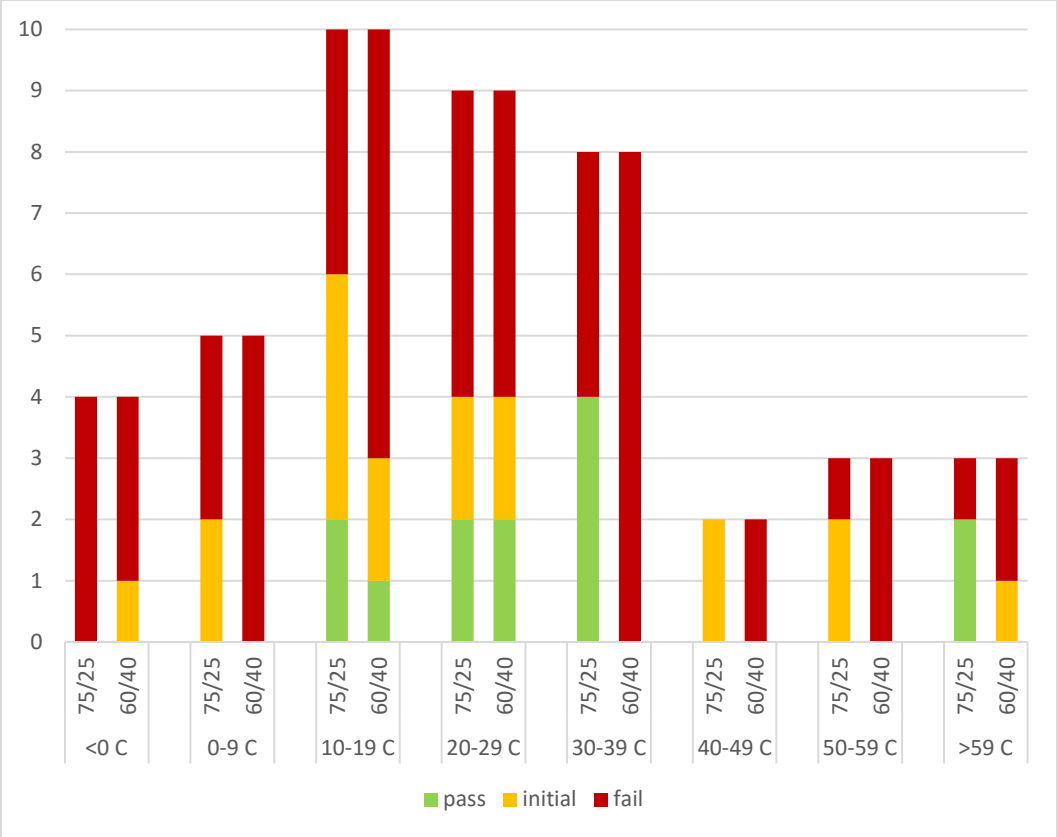

Figure 3-5. Ratings by glass transition temperature of acrylic resins.

3.1.5. Effect of the Minimum Film Formation Temperature

The MFFT, although a property of a latex resin, it is directly affected by the formulation through the use of coalescents. Therefore, in the scope of coatings it is not necessarily a direct property of the resin, though investigation of its possible influence was explored in this study. Forty of the acrylic resins reported their MFFT, the results of these resins grouped by MFFT is shown in Figure 3-6. As can be seen, a passing rating is fairly distributed across the MFFT values. There does not appear to be a correlation.

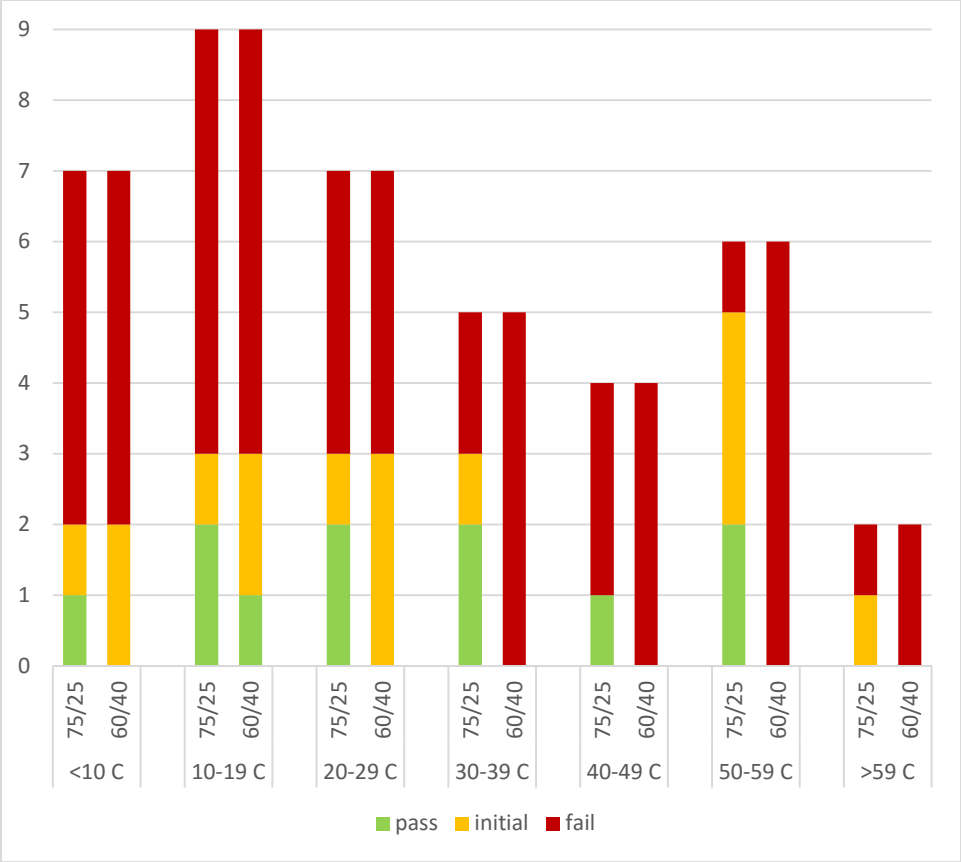

Figure 3-6. Ratings by MFFT of acrylic resins.

3.1.6. Effect of pH

pH is an important consideration with latex resins and water-borne coatings. Therefore it would be expected to have influence in aerosol stability. First, the pH of the resin latex will be examined for trends in rating. Secondly, coating results will be compared to the pH of the formulated concentrate.

Figure 3-7 shows the rating by pH of the resin latex. Looking first at the condensation polymers, there is a noticeable decrease in success as the pH increases in alkalinity. This correlation, however, does not appear to hold with the addition polymers.

There are more passing resins at 7.5 and 8.0, but then the resins with pH in between all failed. No trend can be concluded for latex pH with the addition polymers.

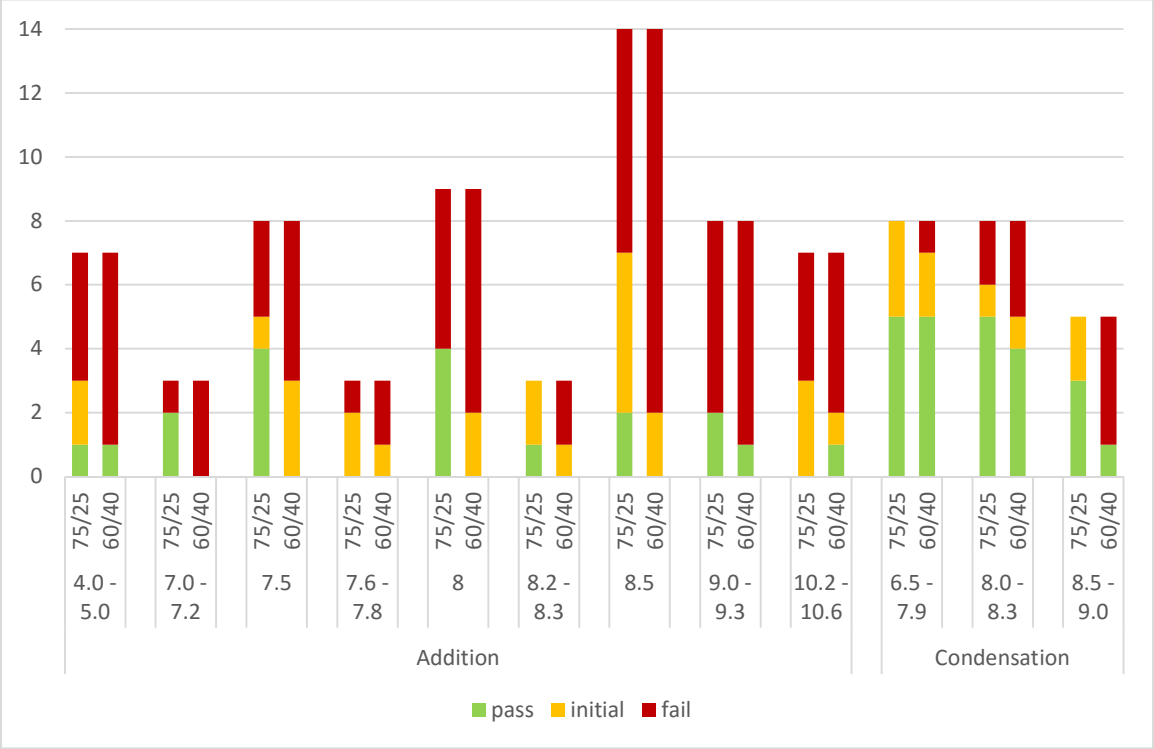

Figure 3-7. Ratings by pH of resin latex.

Ratings by pH of the formulation are shown in Figure 3-8. For condensation polymers a similar trend is seen as above, the rate of success decreases as pH goes up. It could be that for the higher pH resins that failed the pH of the formulation was too high. However, the resins that failed at the high pH end had good drawdown films from the concentrate, which rules out the resin not being stable at those pH levels. This is also true of the addition polymers, the concentrates were stable at the higher pH – the high pH latexes are recommended to maintain the high pH in the formulation. Those resins, however, do

appear to have less success as an aerosol. Aside from a noticeable drop in passing formulations above a pH of 9.5, the addition polymers have less correlation than the condensation polymers.

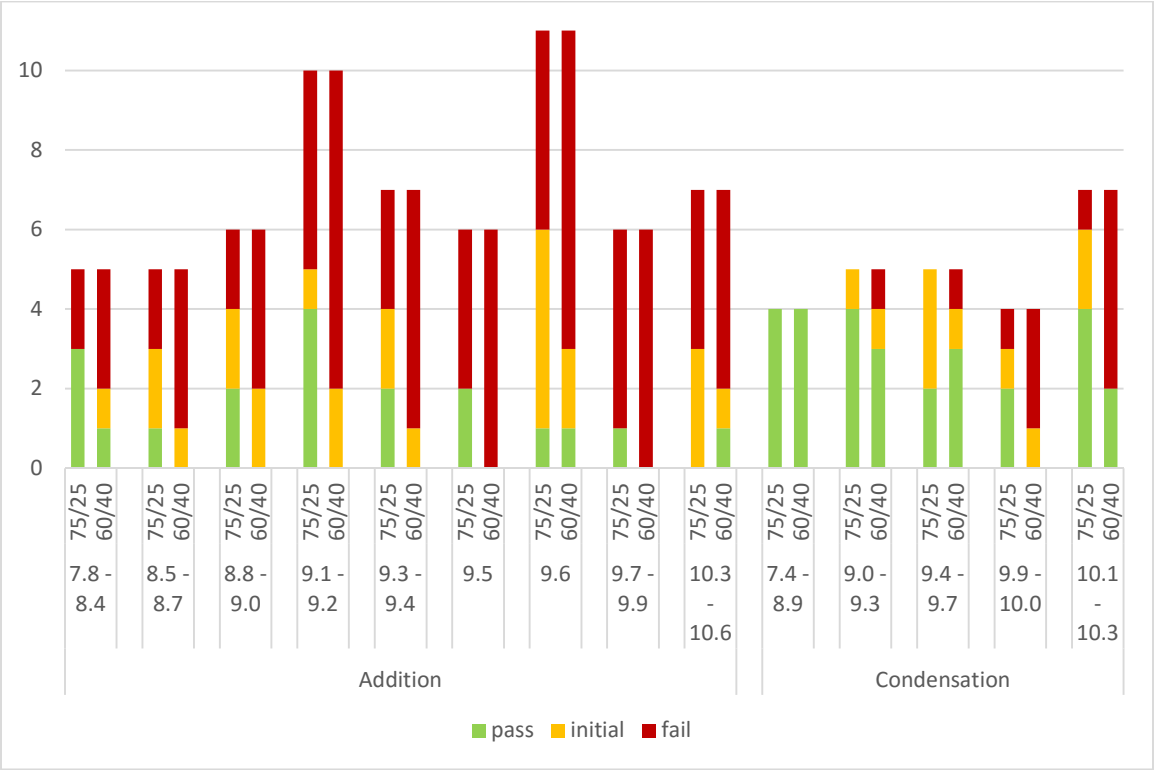

Figure 3-8. Ratings by pH of initial concentrate.

3.1.7. Effect of Concentrate Viscosity Change Upon Aging

The viscosity of a paint concentrate can sometimes change upon aging, though it does not necessitate a failed coating. Many of the concentrates in this study experienced a change in viscosity upon aging, both increases and decreases, yet still produced an acceptable film from the drawdown of the aged sample. The ratings by viscosity change of the concentrate are shown in Figure 3-9. For some of the concentrates the viscometer would not stabilize onto a reading, rather it would oscillate in a range of 2000 – 5000°cP. These

samples are listed in Figure 3-9 as "visc. unstable." With the exception of one outlier, which will be discussed below in Section 3.1.8, all of the samples that had this unstable viscosity were rated as failed. Looking at the rest of the data, the distribution of passing resins is fairly even. Having an unstable viscosity would strongly suggest a formulation that will fail as an aerosol, however outside of this there is no discernable trend.

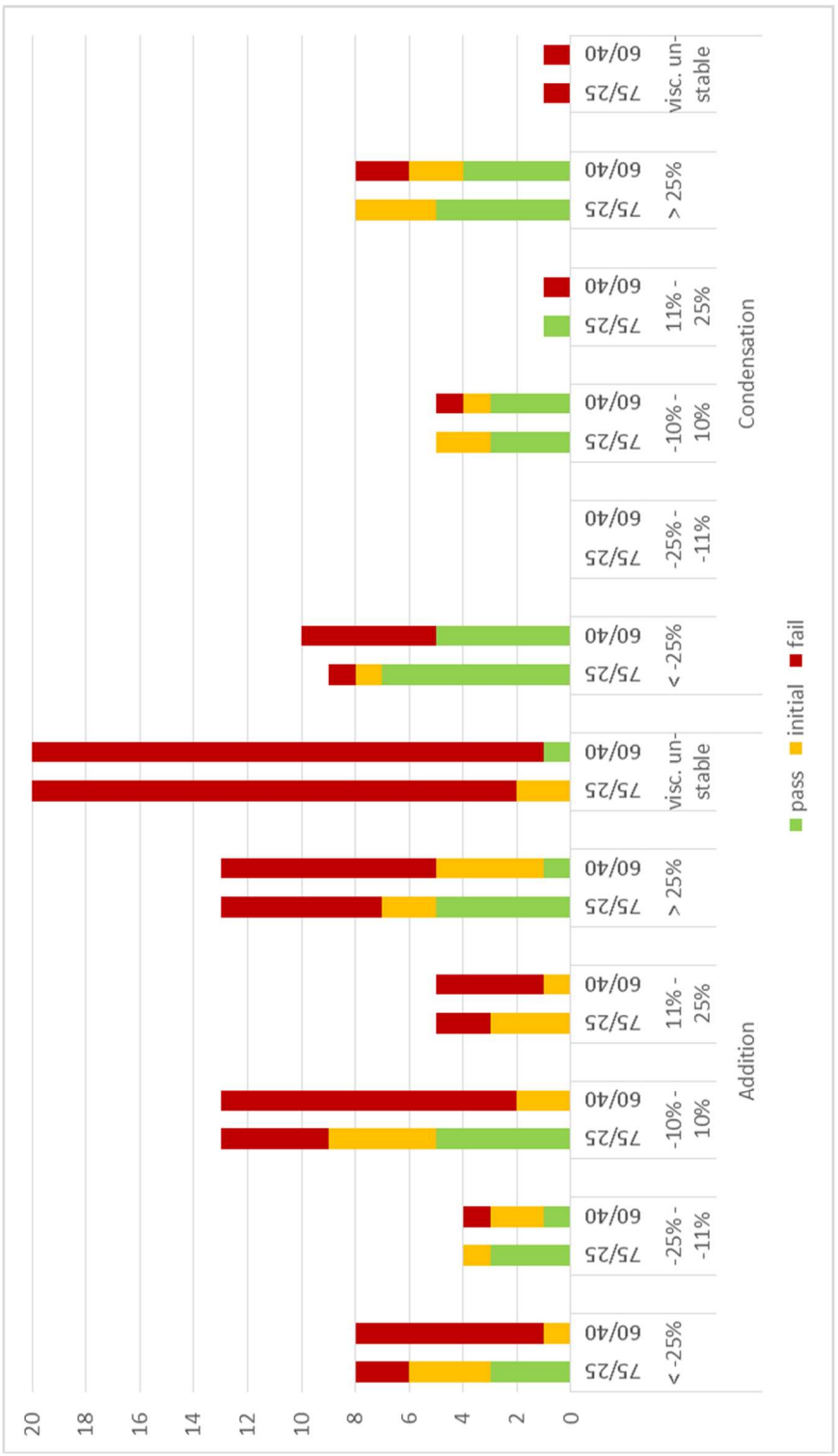

Figure 3-9. Ratings by viscosity change of concentrate upon aging.

3.1.8. Outliers and Other Observations

Seen in all of the data presented, there were more passing ratings for a 75/25 fill ratio than for a 60/40 fill ratio. There were three samples, however, that performed better in the 60/40 fill ratio: RayFlex 777, Fastrack 3427, and Urotuf F600. There is not any obvious correlation or difference about these three from the others within the scope of this study.

Fastrack 3427 was a curious case that deserves further mention. The initial evaluation were usual passing samples. After aging, the concentrate had heterogeneous separation between phases. The drawdown had a blotchy appearance like shown in Figure 2-4, and the viscosity reading was constantly oscillated as mentioned in Section 3.1.7. The spray outs however, produced good, uniform films. The 75/25 sample contained kick out particles which lead to it receiving a failed rating, though the 60/40 spray out had a passing film. It appears that in this instance the DME stabilized the coating.

To add to the curiosity of this, all four of the Fastrack resins in this study are similar, all are 100% acrylics with the same percent solids, pH, and particle size, though there is variance in the T_g of each resin. This highly suggests that the monomer selection and polymerization of the resin is an influential factor in a resin's compatibility with propellant.

Another observation of note is among the alkyd resins. The three that received a passing rating for both fill ratios are all acrylic modified. Urotuf F600, which passed at the 60/40 fill ratio but failed after aging at 75/25, is urethane modified. The other three alkyds, which all failed after aging, are standard alkyds. Long and short oil lengths were represented in the modified and standard resins. It is interesting that most of the acrylics and the standard alkyds failed, yet when a copolymer is comprised of both there was success. This

presents more evidence to the role the polymer itself plays in its stability as an aerosol with DME.

3.2. Stage II

In Stage II five different formulations were made with eight of the resins. The objective was to determine what, if any, affects the formulation had on resin stability with DME. The variables used were two different levels of increased water in the formulation, two different sets of coalescing solvents, and the addition of methanol as a co-solvent for water and DME, all as described in section 2.1.2. The ratings for the resins in each formulation are presented in Table 3-2. As can be seen in the table, three of the resins had no change in performance from the various formulations, no detriment in the cases of Synaqua 821-1377 and Bayhydrol UH 2593/1, and no improvement in the case of Carboset CR-785. The performance of the other resins was affected by changing the formulation and will be discussed further.

Table 3-2. Stage II pass/fail results.

		Formulation					
		I	II.a	II.b	II.c	II.d	II.e
Synaqua 821-1377	75/25	pass	pass	pass	pass	pass	pass
	60/40	pass	pass	pass	pass	pass	pass
Bayhydrol UH 2593/1	75/25	pass	pass	pass	pass	pass	pass
	60/40	pass	pass	pass	pass	pass	pass
EPS 4203	75/25	pass	pass	pass	pass	pass	pass
	60/40	fail	initial	pass	initial	fail	pass
Aquamac 700	75/25	initial	initial	pass	pass	pass	fail
	60/40	fail	fail	fail	fail	fail	fail
Rovene 6131	75/25	pass	pass	pass	fail	initial	fail
	60/40	fail	pass	initial	fail	fail	fail
P-4222	75/25	fail	initial	initial	fail	fail	fail
	60/40	fail	fail	initial	fail	fail	fail
NeoCar 850	75/25	fail	fail	fail	initial	initial	fail
	60/40	fail	fail	fail	fail	fail	initial
Carboset CR-785	75/25	fail	fail	fail	fail	fail	fail
	60/40	fail	fail	fail	fail	fail	fail

Increasing the water content (formulations II.a and II.b) improved the stability of the coating with four of the resins. Aquamac 700 was able to achieve a pass rating where it had failed previously. EPS 4203 and Rovene 6131 both had increased stability with the additional amount of DME with the increased water amount. With P-4222, although it did not pass after aging, it was able to have initial stability where it hadn't before.

A possible explanation for this is the additional water diluted the DME further. If instability was caused by too much DME entering the resin particles, then the additional water may have caused more DME to partition to the aqueous phase. The results for

Rovene 6131 don't necessarily support this since it had a pass rating in formulation II.a but not in II.b. It is possible that some other factor was in play at that further dilution level. It is clear though that increasing the amount of water in the formulation improved the stability of those resins.

Changing the coalescents helped in some cases but hindered in another. Aquamac 700 and NeoCar 850 both saw improvements with both sets of alternate coalescents. Although NeoCar 850 did not receive a pass rating with either formulation II.c or II.d, there was initial stability were there hadn't been in stage I. EPS 4203 saw improved stability in the 60/40 fill ratio with the hydrophilic coalescents, but not with the hydrophobic coalescents. Meanwhile, with Rovene 6131, where it had passed in stage I, it failed with both sets of alternate coalescents. While P-4222 saw improvement with additional water, the coalescent change offered none. Neither set of alternate coalescents showed an overall greater influence than the other.

Like changing coalescents, adding methanol also had mixed results. EPS 4203 and NeoCar 850 both saw improvement with methanol addition. Similar to the resins discussed in section 3.1.8, NeoCar 850 had improved stability in the 60/40 fill ratio but not the 75/25. A decrease in stability was seen with Rovene 6131 and Aquamac 700. No clear trend presents itself regarding methanol addition and appears to be polymer dependent.

The variables tested in stage II produced different results for five of the eight resins included in this stage. No one improved performance in all of the resins, though increasing the water content had the most improvements. The results from stage II show that the

formulation is a factor in a resin's stability in an aerosol, though not in and of itself. The formulation is still resin specific.

4. Summary and Conclusions

Many latex resins were tested for performance as an aerosol coating. Of all the formulations tested, only about one-fourth were successful as a coating. Many factors were investigated in this study to find a relation to success or failure. What was found is that physical properties of the latexes have little to no correlation. Weight percent solids, particle size, and pH of the latex did not prove useful as a means to screen candidate resins.

The results suggest that the primary factor of a latex resin's performance in an aerosol to be with the polymer itself. T_g, a property of a polymer, suggested a better probability for success when within a range of 10 °C – 40 °C. There was also a significant difference in success between resins made through addition polymerization (i.e. acrylic and vinyl polymers) versus condensation polymerization (i.e. alkyd, urethane, and polyester polymers). It is likely that some of the DME is entering the polymer particles and interacting with the polymer. If the reason condensation polymers performed better was because of the ester and urethane bonds in the polymer backbone, DME/polymer solubility could be a factor.

Stage II showed that the formulation can influence a resin's success as an aerosol coating. Three formulations that failed in stage I passed in at least one of the stage II formulations. Though three of the resins in stage II had no difference in performance for any of the stage II formulation, passing and failing resins. Some resins were influenced by

the formulation while others were not. This further supports that the primary factor lies within the polymer itself. It is the goal of the coatings formulator to understand what makes a latex resin a good candidate for use in an aerosol coating. Perhaps though, this is not a question to be answered in the coatings laboratory, but rather the polymer laboratory.

5. Recommendations for Future Work

The results of this study suggest the primary influence of a latex resin's success as an aerosol coating lies within the polymer. As such, that is where the focus of future work should be. There is bound to be (or at least coatings formulators can hope) some correlation by polymer structure.

There are many, many monomers available for polymer creation and near infinite possibilities of combining monomers. For example, methyl acrylates may lead to better performing polymers than acrylates. Perhaps what differentiated the successful acrylic resins in this study was the use of a common pendant group that was absent from the others. It was seen above that within the alkyd resins, the acrylic modified ones performed the best. Further investigation to confirm or disprove this as a trend would be informative.

Addition polymers have polymerization initiators at the ends of the polymer chains. If the initiator interacts with DME impacting the stability of the resin, then initiator choice would be important for making latex resins for aerosol coatings. Research into this would further illuminate the issue.

Another possible area to investigate is the polymerization surfactant. It is possible the DME is interacting with the surfactant leading to the destabilization of the resin. A trend

could be discovered in choice of polymerization surfactant to success in an aerosol. If a correlation is found, adding additional surfactant at the formulation level may be able to mitigate the destabilization.

Coatings and polymers have many interrelated parts and questions in coatings generally do not have a simple answer. The results of this study may not have provided concrete answers, but it has provided direction on how to proceed forward in growing our understanding. Perhaps one day water-borne coatings will be as prevalent in aerosols as they currently are in brushing paints.

6. References

[1] Leep, G. W. Water-Borne Aerosol Coating Composition. WO 1997034954, September 25, 1997.

[2] Rapaport, S. and Cachat, F. J. Water Reducible Aerosol Paints. US 4420575 A, December 13, 1983.

[3] Suk, A. Aerosol Water-Based Paint Composition. US 4265797 A, May 5, 1981.

[4] Wicks, Z. W. *Organic Coatings: Science and Technology*, 3rd Ed.; Wiley-Interscience: Hoboken, 2007.

[5] Davison, G. and Lane, B. *Additives in Water-Borne Coatings*; Royal Society of Chemistry: Cambridge, 2003.

[6] Harkins, W. D. A General Theory of the Reaction Loci in Emulsion Polymerization. *Journal of Chemical Physics*. 1945, 13, p.381.

[7] Smith, W. V. and Ewart, R. H. Kinetics of Emulsion Polymerization. *Journal of Chemical Physics*. 1948, 16, p.592.

[8] Harkins, W. D. A General Theory of the Mechanism of Emulsion Polymerization. *Journal of the American Chemical Society*. 1947, 69, p.1428.

[9] Ausa, J. M. Miniemulsion Polymerization. *Progress in Polymer Science*. 2002, 27, p.1283.

[10] Kalendov´a, A.; Kalenda, P.; Vesel´y, D. Comparison of the Efficiency of Inorganic Nonmetal Pigments with Zinc Powder in Anticorrosion Paints. *Progress in Organic Coatings*. 2006, 57, p.1

[11] Turner, G. P. A. *Paint Chemistry and Principles of Paint Technology*, Chapman and Hall: New York, 1988.

[12] Weidner, D. E., Schwartz, L. W., and Elay, R. R. Role of Surface Tension Gradients in Correcting Coating Defects in Corners. *Journal of Colloid and Interface Science*, 1996, 179, p.66.

[13] Lambourne, R. Ed. *Paint and Surface Coatings: Theory and Practice*, Ellis Horwood Limited: Chicester, 1987.

[14] Provder, T. and Urban, M. W. *Film Formation in Coatings: Mechanisms, Properties, and Morphology*; American Chemical Society: Washington, D.C., 2001.

[15] Pruskowski, Jr. S. J. Ed. *Waterborne Coatings Technology*, Federation of Societies for Coatings Technology: Blue Bell, 2004.

[16] Shepherd, H. R. Ed. *AEROSOLS: Science and Technology*, Interscience Publishers, Inc.: New York, 1961.

[17] Seymour E.H. Hermetically sealed package for mixing and discharging paint. US2580132 A, December 25, 1951.

[18] Johnsen, M. A. *The Aerosol Handbook*, 2nd ed.; Wayne Dorland Company: Mendham, 1982.

[19] Chadwick, J., Particle Size Control in Aerosol Packages. *Spray technology and Marketing*. December, 2004.

[20] Chadwick, J., Controlling Particle Size in Self-Pressurized Aerosol Packages. *Metal Finishing*, July/August 2004.

[21] Sanders, P. A. *Handbook of Aerosol Technology*, 2nd ed., Van Nostrand Reinhold Company: New York, 1979.

[22] Shaik, N. B. Pharmaceutical Aerosols. http://www.pharmainfo.net/book/pharmaceutical-aerosols/definition-advantagesand-disadvantages (accessed March 10, 2016)

[23] Hipkin, H. Experimental Vapor-Liquid Equilibrium Data for Propane-Isobutane. *AIChE J.* 1966, 12, p.484-487.

[24] Maczynski, A., Goral, M., Wisniewska-Goclowska, B., Skrzecz, A., and Shaw, D. Mutual Solubilities of Water and Alkanes. *Monatshefte für Chemie*. 2003, 134, p.633-653.

[25] Wu, J., Yin, J. Vapor Pressure Measurements of Dimethyl Ether from (213 to 393) K. *Journal of Chemical and Engineering Data*. 2008, 53, p.2247-2249.

[26] Guomin, J., Johnsen, M. A., Braune, B. V. *Aerosol Propellant Handbook*; Cosmos Books LTD: Honk Kong, 1998.

Vita

Brian Robert Gosselin was born on November 5, 1981in Tacoma, WA to David and Paula Gosselin of Tacoma, WA. Raised in Tacoma, Brian attended Bellarmine Preparatory School, graduating in 2000. He then attended Easter Washington University in Cheney, WA, pursued a B.S in Chemistry, graduating magna cum laude with university honors in 2004. Brian entered the coatings industry in 2009 with Testor Corp. and currently works for Seymour of Sycamore. He received a M.S. in Polymer Science and Engineering from Lehigh University in May 2016.